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The Effect of Vibrational Excitation of Molecules on Plasmachemical Reactions Involving Methane and Nitrogen

Sergey Y. Savinov,[2] Hwaung Lee,[1] Hyung Keun Song,[1] and Byung-Ki Na[1,3]

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An experimental study of plasmachemical reaction involving CH_4 and N_2 molecules in rf discharge was studied in order to know the effect of vibrational excitation of N_2 molecules. When the relative nitrogen concentration was greater than 0.8, the main product of CH_4 decomposition was HCN, and the rate of methane decomposition at this condition was faster than that one in pure methane. These results could be confirmed through the mass spectroscopic method. The reason for these results is the vibrational energy of N_2 excited by rf discharge. The chain reaction mechanisms of producing HCN by vibrational excitation of N_2 were examined closely through numerical simulation. The rate-controlling step was the dissociation reaction of excited nitrogen molecule to the atomic nitrogen, so the process of HCN synthesis was limited by the value of reaction constant, k^N.

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KEY WORDS: rf discharge; methane; nitrogen; HCN; vibrational excitation; mechanism.

1. INTRODUCTION

Studies of chemical reactions in non-equilibrium molecular plasma at elevated pressures have been closely related to the progress of plasmachemistry, hydrogen power engineering, waste-handling of natural gases, cleaning of an environment, etc. The energy efficiency of non-equilibrium plasmachemical process depends on the set of channels it flows, i.e., on the mechanism of the process. It has been known that the vibrational excitation of molecules essentially accelerates endothermic chemical reactions.(1) However, it is not always possible to excite the required vibrational mode of

[1]Clean Technology Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, 130-650, Korea.
[2]Low Temperature Plasma Optics Department, P. N. Lebedev Physical Institute, Leninsky Prosp. 53, Moscow, 117924, Russia.
[3]To whom correspondence should be addressed. email: nabk@kist.re.kr

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molecules selectively by an electric discharge. In our previous work,[2,3] we investigated the decomposition of pure methane and carbon dioxide in a radio-frequency discharge. It was shown that the dissociation of these molecules was due to the excitation of electronic states. The plasmachemical reactions in nitrogen mixtures were examined in order to analyze the effect of vibrational excitation on the reactions involving methane.

Molecular nitrogen has a large effective cross section of the vibrational levels excited by electron impact ($3 \times 10^{-16}\,cm^2$), a small effective cross section of vibrational relaxation ($3 \times 10^{-24}\,cm^2$) and a small factor of the vibrational energy loss on the surfaces. For glass, quartz, stainless steel and copper, this factor for the accommodation of vibrational energy loss is equal to about 10^{-3}.[1] In other words, N_2 molecules are excited in discharge very easily and act as a reservoir of the vibrational energy.

2. EXPERIMENTAL

We investigated the plasmachemical reactions involving CH_4 and N_2 molecules in radio-frequency discharge ($\nu = 13.56\,MHz$) by a mass spectroscopic method. These reactions took place in discharge in the gas mixtures of CH_4 and N_2. We used a special type of capacitive discharge. A similar discharge system was applied at first for the design of CO_2 lasers by Yatsenko[4] and was later used in this experiment for plasmachemical purposes.[2]

The schematic drawing of the experimental setup was shown in Fig. 1. Plasmachemical reactor consists of a long pyrex (or quartz) tube. Four copper wires were located on the outside tube and were used as electrodes. The diameter of each wire was $d/10$, where d is the inner diameter of the reactor. Any two of these were connected with power supply and the other two were connected to earth. The reactor was made of Pyrex glass with an internal diameter of 12 mm and a total length of 700 mm, and the plasma zone had 500 mm length. More detailed descriptions of the plasmachemical reactor and all experimental equipment were described in our previous work.[2] The main peculiarity of these reactors was the small sizes of the electrode sheathes. As a result almost all volume of the discharge tube was filled with positive column plasma.[4] The pressure of gas mixture was changed from 5 to 60 torr.

The radio-frequency generator with a matching network delivered an output power from 0 to 300 W. The magnitude of reflected power did not exceed 2% from the delivered one. The maximum of unique power for the reactor was about $7.2\,W/cm^3$. While measuring discharge input power, we ignored the energy loss through radiation and, furthermore, we suggested that all input power was absorbed by positive column plasma.

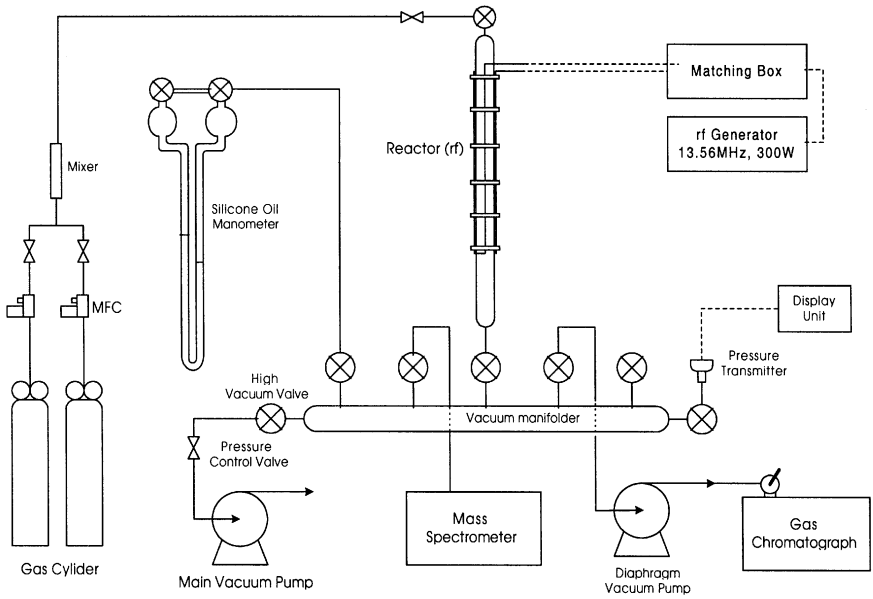

Fig. 1. Schematic drawing of the experimental setup.

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CH_4 and N_2 with 99.9% purity were used. Quadrapole mass spectrometer (Balzers, QMS 200) with Quadstar 421 software was used for qualitative and quantitative analysis of the gas mixtures. Mass spectrometer was connected to the post discharge zone. Gas mixture in this zone was maintained at room temperature. Before measurements, we carried out a calibration of the mass spectrometer with the data based on the mass spectrum of the binary mixtures. CH_4, C_2H_6, C_2H_4, C_3H_8, and Ar gases with 99.9% purity were used for the calibration.

Some expressions in our previous work[2] were used to define the conversions of initial reactants and molecular flows of reactants and products investigated. The residence time was considered for the change of the flow-rate by chemical reactions.

3. RESULTS AND DISCUSSION

Let us consider plasmachemical reactions in discharge in mixture of CH_4 and N_2. The effect of relative nitrogen concentration ($\beta_{N_2} = [N_2]^0/[N_2]^0 + [CH_4]^0$, here $[N_2]^0$ is the initial concentration of the nitrogen molecules and $[CH_4]^0$ is the initial one of the methane molecules) was investigated on plasmachemical processes. The mass spectra analysis

showed that the influence of nitrogen was minor for $\beta_{N_2} < 0.65$. The situation was very similar to the discharge in pure methane.[2] At low input power of 120 W ethane and hydrogen were the main products. As the input power was increased, the unsaturated groups of C_2 and C_3 began to form. At $\beta_{N_2} > 0.8$ the situation was quite different. The main products of CH_4 decomposition were HCN and H_2. No other substances were detected in noticeable amounts.

At $\beta_{N_2} > 0.8$ the main plasmachemical process in the discharge is as follows:

$$CH_4 + \tfrac{1}{2}N_2 \rightarrow HCN + \tfrac{3}{2}H_2 \qquad (1)$$

As an illustration of this process, the dependencies of the methane conversion and the ratio of $\hat{F}^{Pr}_{H_2}/\hat{F}^{R}_{CH_4}$ at relative nitrogen concentration are presented in Figs. 2 and 3 under various input powers. Here, $\hat{F}^{Pr}_{H_2}$ is the flow rate of the molecular hydrogen in the post-plasma zone, $\hat{F}^{R}_{CH_4}$ is that of the methane molecules in the chemical reaction zone. Initial conditions were that total pressure $P_1(0)$ was 23 torr and total flow rate V^0 was 55 cm^3/min. It should be noted that the methane conversion increased as the value of β_{N_2} increased. At $\beta_{N_2} = 0.9$ and $W \geq 200$ W almost all methane was converted into HCN and H_2 ($Z_{CH_4} > 0.9$, where Z_{CH_4} is the conversion of methane).

The ratio of $\hat{F}^{Pr}_{H_2}/\hat{F}^{R}_{CH_4}$, was almost constant at $W \geq 200$ W, and the value was equal to 1.5 as shown in Fig. 3. At 120 W of input power and

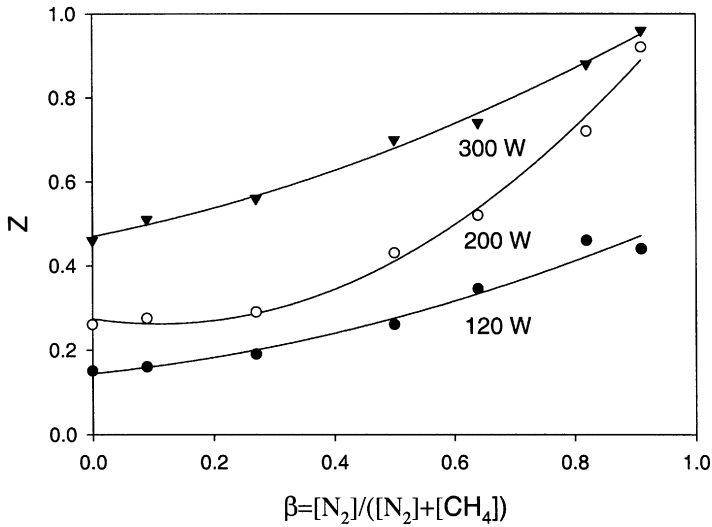

Fig. 2. The dependencies of methane conversion Z on relative nitrogen concentration for 3 values of input power. The initial conditions were: discharge in mixture CH_4–N_2, total pressure is $P_1(0) = 23$ torr, and total flowrate $\hat{V}^{(0)} = 55$ cm^3/min.

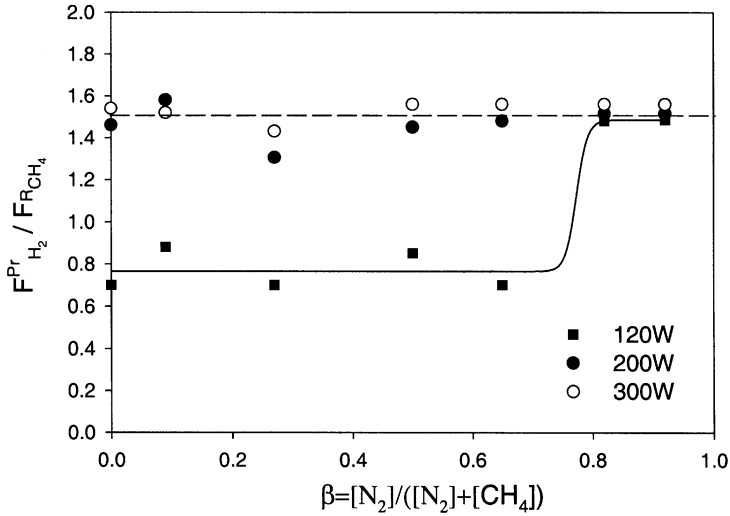

Fig. 3. The dependency of the ratio $\hat{F}^{Pr}_{H_2}/\hat{F}^{R}_{CH_4}$ on relative nitrogen concentration for 3 values of input power. The initial conditions were: discharge in mixture CH_4–N_2, total pressure $P_1(0) = 23$ torr, and total flowrate $\hat{V}^{(0)} = 55\,cm^3/min$.

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$\beta_{N_2} < 0.65$ the value of $\hat{F}^{Pr}_{H_2}/\hat{F}^{R}_{CH_4}$ was equal to about 0.8. At $\beta_{N_2} > 0.8$ this value was equal to 1.5. In the region of $0.65 < \beta_{N_2} < 0.8$, it showed a drastic change of $\hat{F}^{Pr}_{H_2}/\hat{F}^{R}_{CH_4}$ from 0.8 to 1.5. The reaction mechanisms changed in this region. If $\beta_{N_2} < 0.65$ the nitrogen molecules were not involved in plasmachemical reactions, but at $\beta_{N_2} > 0.8$ the chain reaction occurred as follows:[1]

$$CH_4 + N \xrightarrow{k^{HCN}} HCN + H_2 + H, \qquad \Delta H = -0.51\ eV \tag{2}$$

$$H + N_2^* \xrightarrow{k^{N}} NH + N, \qquad E_a \cong \Delta H = 6.54\ eV \tag{3}$$

$$NH + NH \xrightarrow{k^{N2}} N_2 + H_2, \qquad \Delta H = -7.8\ eV \tag{4}$$

where ΔH is the standard enthalpy of the reaction, and E_a is the activation energy of the reaction. It can be shown that the next combined rate equations describe this mechanism (2)–(4):

$$-\frac{d[CH_4]}{dt} = k^{HCN}[N][CH_4] \tag{5}$$

$$\frac{d[N]}{dt} = k^{N} C_1 [N_2] - (k^{N}[N_2] + k^{HCN}[CH_4])[N] \tag{6}$$

$$\frac{d[N_2]}{dt} = k^{N_2}[NH]^2 - k^N(C_1 - [N])[N_2] \tag{7}$$

$$\frac{d[NH]}{dt} = k^N(C_1 - [N])[N_2] - 2k^{N_2}[NH]^2 \tag{8}$$

where the values in the square bracket are the concentration of the relevant substances, k^{HCN}, k^N, and k^{N_2} are the rate constants of reactions (2)–(4), C_1 is a constant value. (It can be derived from reactions (2)–(4) that $C_1 = [N] + [H]$.)

It is obvious, that

$$[HCN] = [CH_4]^0 - [CH_4] \tag{9}$$

where $[CH_4]^0$ is the initial concentration of methane molecules (that is, $[CH_4]^0$ is the concentration in the predischarge zone), and $[CH_4]$ is the current concentration.

Let us consider the peculiarities of the processes (2)–(4). It is easy to understand that the synthesis is limited by endothermic reaction (3). This reaction is stimulated by vibrational excitation of nitrogen molecules quite well. It is a reasonable assumption that $k^N \ll k^{HCN} \sim k^{N_2}$.

The effect of atomic-nitrogen concentration is our primary concern. From Eq. (6), we can find

$$[N] = \frac{k^N C_1[N_2] - C_2 \exp(-(k^N[N_2] + k^{HCN}[CH_4])t)}{k^N[N_2] + k^{HCN}[CH_4]} \tag{10}$$

Where C_2 is a constant value defined from the initial condition of $[N(t = 0)] = [N]^0$. From Eq. (10), it may be seen that under the condition of

$$t > t_1 = (k^N[N_2] + k^{HCN}[CH_4])^{-1} \tag{11}$$

the atomic–nitrogen concentration will be

$$[N]_1 = \frac{k^N[N_2]C_1}{k^{HCN}[CH_4] + k^N[N_2]} \tag{12}$$

at any initial conditions. If

$$k^{HCN}[CH_4]^0 \gg k^N[N_2]^0, \qquad t_1 = (k^{HCN}[CH_4])^{-1} \quad \text{and} \quad [N]_1 = \frac{k^N}{k^{HCN}} \frac{[N_2]}{[CH_4]} C_1.$$

Let us consider now the rate equation (5) for the methane concentration. From Eq. (5), the time scale of the substantial methane concentration change is $\tau \sim (C_1 k^{HCN})^{-1}$, where τ is the residence time of the reactor. Notice that it is estimation for the minimum time.

In the conditions of the molecular gas discharge plasma, the concentrations of atomic species are much less than the initial concentrations of the molecular species.[6] Hence, the residence time is greater than t_1 ($\tau \gg t_1$), the concentrations of $[CH_4]$ and $[N_2]$ are almost the same during the period of time from 0 to t_1. It means that we can substitute the initial values of $[CH_4]^0$ and $[N_2]^0$ into Eq. (12) and the value of $[N]_1$ from Eq. (12) into Eq. (5), thus we have the next equation,

$$\frac{d[CH_4]}{[CH_4]} = k^N \frac{[N_2]^0}{[CH_4]^0} C_1 \, dt \tag{13}$$

From the Eq. (13), the methane concentration decreases by the following equation,

$$[CH_4] = [CH_4]^0 \exp\left\{-k^N C_1 \frac{[N_2]^0}{[CH_4]^0} t\right\} \tag{14}$$

with the characteristic time,

$$t_2 = \frac{1}{k^N C_1} \frac{[CH_4]^0}{[N_2]^0} \tag{15}$$

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It is necessary to point out that t_2 is the time for the HCN production (Eq. (2)).

Thus, as mentioned in the above relations, the plasmachemical process of HCN synthesis was independent of the initial value of $[N]^0$. During the time period of order of $t_1 \sim (k^{HCN}[CH_4]^0)^{-1}$, the concentration of atomic nitrogen defined by Eq. (12) is used in the system under investigation. The densities of $[CH_4]^0$ and $[N_2]^0$ do not change practically during this time. Then during the time period of order

$$t_2 \sim \left(\frac{1}{k^N C_1} \frac{[CH_4]^0}{[N_2]^0}\right) \gg t_1$$

the concentration of methane molecules decreases noticeably. (In this time the noticeable amount of [HCN] is produced.) It is obvious that for $\tau \gg t_2$, when the concentration of CH_4 decreases significantly, the value of [N] will be equal to C_1 (see Eq. (12)) and the concentration of $[CH_4]$ will decrease by the following relation,

$$[CH_4] \sim \exp(-k^{HCN} C_1 t_1) \tag{16}$$

with the characteristic time of $\tau = (k^{HCN} C_1)^{-1}$.

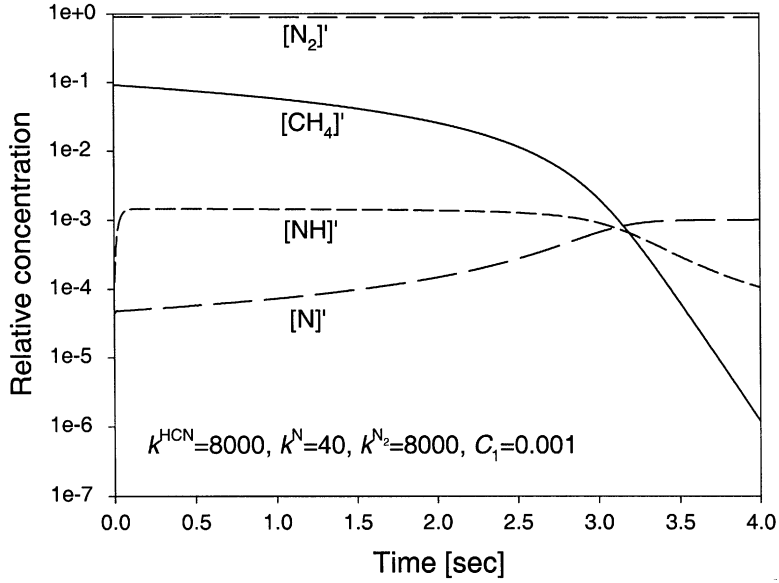

Fig. 4. The time on stream of N_2, CH_4, NH, and N concentrations. The initial conditions were: $[CH_4]^{0\prime} = 0.091$, $[N]^{0\prime} = 10^{-6}$, $[N_2]^{0\prime} = 0.091$, and $[NH]^{0\prime} = 10^{-7}$.

For the examination of the above estimations, we made a numerical modeling of the process described by Eqs. (5)–(8). To make a simple analysis more easy we introduce the new variables for the concentrations and the rate constants, $[\,]' = [\,]/[CH_4]^0 + [N_2]^0$. The unit of $[\,]'$ is dimensionless.

In order to solve these equations, we used the Runge–Kutta method. The initial densities were $[CH_4]^{0\prime} = 0.091$, $[N_2]^{0\prime} = 0.91$, $[NH]^{0\prime} = 0$, and the concentration of atomic nitrogen $[N]^{0\prime}$ was changed. All results are presented in a graphical form with dependence of $\ln[\,]'$ on time. In the condition under investigation ($P_R = 23$ torr, $V^0 = 55\,cm^3/min$, $T_R = 800\,K$) the mean residence time for molecules in plasma was about $\tau = 0.5$ sec, which was defined as the characteristic time scale.

Figures 4 and 5 show the dependencies of results on initial value of $[N]^{0\prime}$. For Fig. 4 the value of the nitrogen atom concentration was $[N]^{0\prime} = 10^{-6}$, and for Fig. 5 that one $[N]^{0\prime} = C_1 = 10^{-3}$. From these figures two results were obtained.

Firstly, practically there is no influence of the initial density of the nitrogen atoms on the time dependency of $[CH_4]'$ (or on the time dependency of [HCN]). Secondly, it is possible to use the simple estimation for the times $t_1 = 1.4 \times 10^{-3}$ sec and $t_2 = 2.5$ sec from Eqs. (11) and (15).

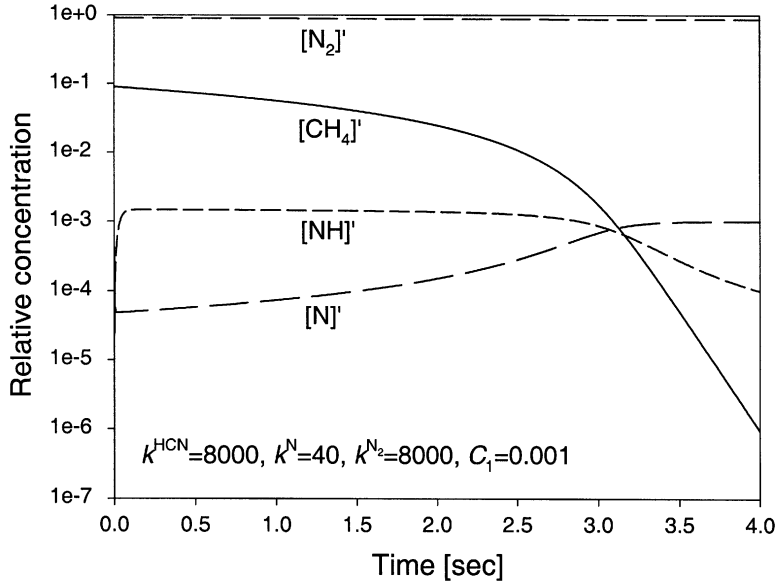

Fig. 5. The time on stream of N_2, CH_4, NH, and N concentrations to show the influence of $[N]^{0\prime}$. The initial conditions were: $[CH_4]^{0\prime} = 0.091$, $[N]^{0\prime} = C_1 = 10^{-3}$, $[N_2]^{0\prime} = 0.91$, and $[NH]^{0\prime} = 10^{-7}$.

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Figure 6 shows the effect of the rate constants of k^{HCN} and k^{N_2} with the reaction time. In this figure the values of k^{HCN} and k^{N_2} were greater than those in Figs. 4 and 5 by a factor of 10. These figures showed that the time of t_2 in Fig. 6 was approximately equal to those in Figs. 4 and 5. When the value of [N]′ was equal to $C_1 = 0.001$, the rate of the methane decomposition increased more sharply in Fig. 6 than Figs. 4 and 5. But this fact had no practical importance, because the methane concentration had decreased at this moment by two orders of magnitude (i.e., the methane was almost decomposed) and most of HCN had been produced. Hence the process of HCN synthesis is not strongly affected by the values of k^{HCN} and k^{N_2}.

Figure 7 demonstrates the effect of the value of k^N as time goes by. In this figure k^N was increased by a factor of 4 in comparison with previous figures. The time $t_2 = 0.63$ decreased accordingly by a factor of 4, and the production of HCN was accelerated noticeably.

Up to this point, we considered that $k^{HCN} = k^{N_2}$. Figures 8 and 9 demonstrate that this assumption is not crucial. In conditions under investigation, when the value of $[N_2]$ is noticeably greater than the value of $[CH_4]$, the value of k^{N_2} has no practical effect on time evolution of the methane

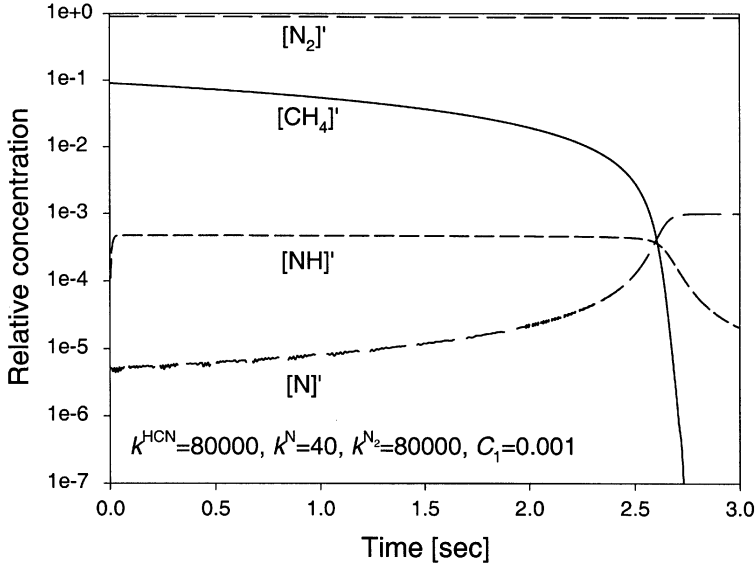

Fig. 6. The time on stream of N_2, CH_4, NH, and N concentrations to show the influence of values of k^{HCN} and k^{N_2}. The initial conditions were: $[CH_4]^{0\prime} = 0.091$, $[N]^{0\prime} = 10^{-3}$, $[N_2]^{0\prime} = 0.91$ and $[NH]^{0\prime} = 10^{-7}$.

decomposition. $k^{N_2} = 180{,}000\ \text{sec}^{-1}$ in Fig. 8 and $k^{N_2} = 8000\ \text{sec}^{-1}$ in Fig. 9. Nevertheless the time of changing $[CH_4]$ and [N] are the same for these figures. The value of k^{N_2} has an effect only on the value of the intermediate product density, [NH], but has no noticeable effect on the rate of decomposition.

Thus the results of the numerical modeling supported the validity of the estimations which were made on the basis of the simplified consideration.

In our previous work,[2] we obtained the expression for describing methane decomposition process in discharge with the pure methane. In that case, the methane-concentration change was described as follows

$$[CH_4] = [CH_4]^0 \exp\{-n_e(v_e\sigma^e_{\text{diss}})t\} \tag{17}$$

where t is the residence time. The frequency of collisions for methane molecules with electrons is $n_e(v_e\sigma^e_{\text{diss}})$ where n_e is the density of electrons, v_e is the speed of electrons and σ^e_{diss} is an effective cross section for dissociation by direct electron impact.

A comparison between Eq. (17) and Eq. (14) shows that the methane concentration decays exponentially in discharge with pure methane and with

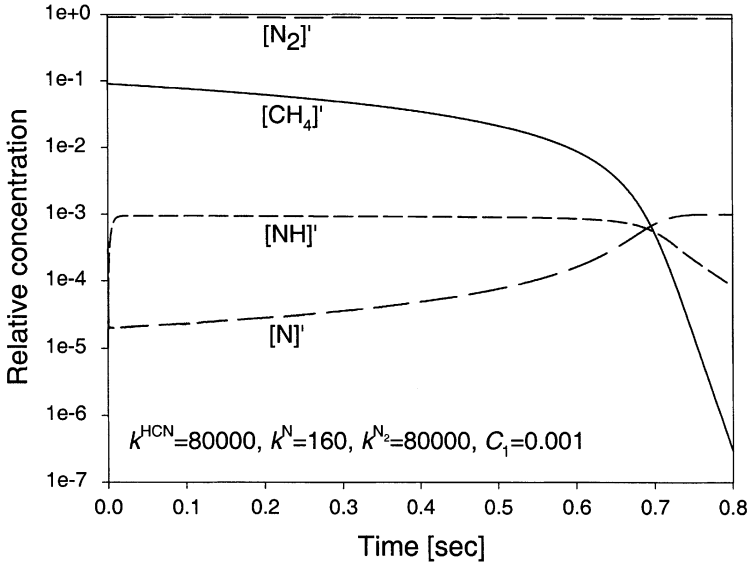

Fig. 7. The time on stream of N_2, CH_4, NH, and N concentrations to show the influence of values of k^N. The initial conditions were: $[CH_4]^{0\prime} = 0.091$, $[N]^{0\prime} = C_1 = 10^{-3}$, $[N_2]^{0\prime} = 0.91$, and $[NH]^{0\prime} = 10^{-7}$.

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the mixture of CH_4 and N_2. If

$$n_e(v_e\sigma^e_{\text{diss}}) > k^N C_1 \frac{[N_2]^0}{[CH_4]^0}$$

the nitrogen molecules are not involved in plasmachemical process. If

$$n_e(v_e\sigma^e_{\text{diss}}) < k^N C_1 \frac{[N_2]^0}{[CH_4]^0}$$

the mechanisms of (2)–(3) are significant and nitrogen molecules are involved in chemical reactions.

If $\beta_{N_2} < 0.65$ the nitrogen molecules were not involved in plasmachemical reactions. The production of nitrogen atoms was too small. But at $\beta_{N_2} > 0.8$ the chain reaction occurred. The reaction mechanisms changed in the region of $0.65 < \beta_{N_2} < 0.8$. The discussed mechanism was not influenced by the total concentration of nitrogen and hydrogen atoms ($C_1 = [N] + [H]$). The presence of initial nitrogen and hydrogen atoms in plasma could be determined by the electron impact dissociation of N_2 and H_2. But it should be mentioned that the electron impact dissociation of N_2 in rf discharge could not play the main role in the production of

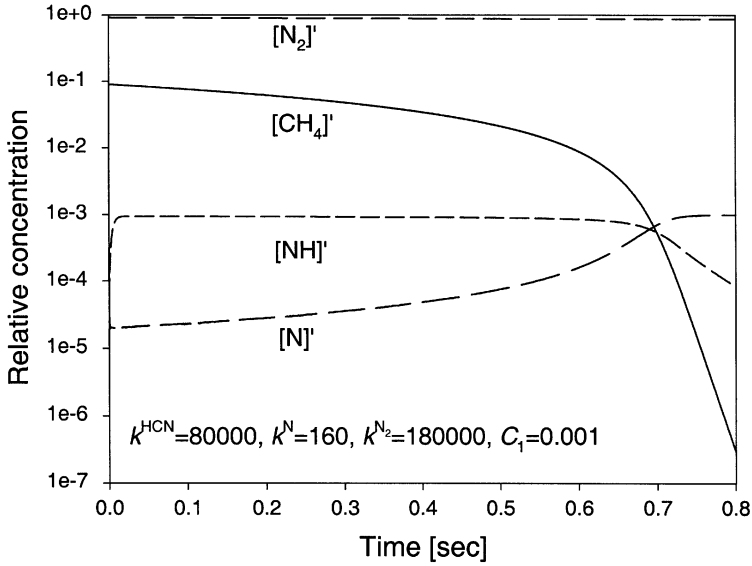

Fig. 8. The time on stream of N_2, CH_4, NH, and N concentrations to show the influence of values of k^{HCN} and k^{N_2}. The initial conditions were: $[CH_4]^{0\prime} = 0.091$, $[N]^{0\prime} = C_1 = 10^{-3}$, $[N_2]^{0\prime} = 0.91$, and $[NH]^{0\prime} = 10^{-7}$.

N atoms at the condition under investigation. The efficiency of electron impact dissociation depended on the parameters of gas discharge. The reduced electric field strength E/N (E is the longitudinal electrical field strength and N is the density of neutral plasma gas particles) was one of major parameters. This parameter determined the mean energy of electrons in plasma and, accordingly, the energy balance of different degrees of freedom of the atomic and the molecular components in plasma. But under changing β_{N_2} from 0.65 to $0.8\,E/N$ changed very lightly and the efficiency of electron impact dissociation could not rise noticeably in this region.

It is necessary to point out that the dissociation energy of N_2 is higher than the bond dissociation energy of CH_3–H by a factor of 2. Nevertheless under favorable conditions the N_2 is excited easily up to high vibrational levels. The presence of many vibrational excited molecules noticeably increases the value of k^N. When

$$n_e(v_e\sigma^e_{\text{diss}}) < k^N C_1 \frac{[N_2]^0}{[CH_4]^0}$$

the chain mechanism of (2)–(4) began to dominate and the synthesis of HCN took place in the plasma. Because $k^N C_1([N_2]^0/[CH_4]^0)$ was noticeably

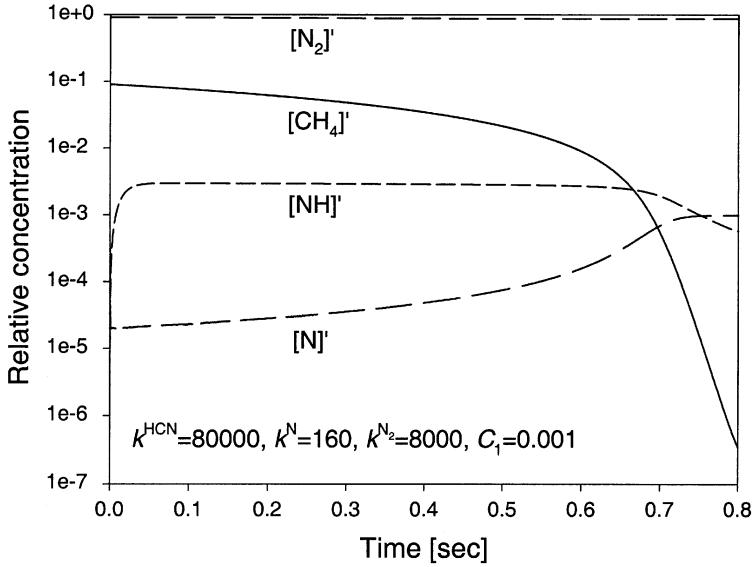

Fig. 9. The time on stream of N_2, CH_4, NH, and N concentrations to show the influence of values of k^{HCN} and k^{N_2}. The initial conditions were: $[CH_4]^{0\prime} = 0.091$, $[N]^{0\prime} = C_1 = 10^{-3}$, $[N_2]^{0\prime} = 0.91$, and $[NH]^{0\prime} = 10^{-7}$.

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larger than $n_e(v_e \sigma^e_{diss})$ in this condition, the transition to this mode of discharge operation had to be accompanied by the increase of the methane conversion.

4. CONCLUSIONS

An experimental study of plasmachemical reaction involving CH_4 molecules with N_2 in rf discharge was investigated with a mass spectroscopic method. When the relative nitrogen concentration was greater than 0.8, the main product of CH_4 decomposition was HCN. However, the other conditions, especially the relative N_2 concentration was less than 0.6, the reaction mechanism was almost the same as the decomposition of pure CH_4.

The chain reaction mechanisms of producing HCN by vibrational excitation of N_2 were examined closely through experiments and numerical simulation. The rate-controlling step was the dissociation reaction of excited nitrogen molecule to the atomioc nitrogen. As a result, practically there was no influence of the initial concentration of the nitrogen atoms on the time dependency of CH_4 or HCN concentration.

When the value of rate constant, k^N, increased, the reaction time decreased accordingly and the production of HCN was accelerated noticeably. Hence the process of HCN synthesis was induced which was limited by the value of k^N. The values of k^{HCN} and k^{N_2} affected only the concentration of NH, but have no noticeable effect on the rate of decomposition.

In the frame of this work we had no possibility of defining the values of C_1 and k^N. By using Eq. (14) and the value of mean residence time for molecules in plasma ($\tau = 0.5$ sec) we could obtain information about the product of $C_1 k^N \sim 0.5\ s^{-1}$. In the future it will be interesting to make special experiments to measure the vibrational temperature of N_2 and to estimate the atomic concentration in the plasma. It enables us to obtain new information about the process under investigation.

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NOMENCLATURE

C_1 = constant, [H] + [N]
E_a = activation energy, eV
$\hat{F}$ = flow of molecular spices, min^{-1}
ΔH = standard enthalpy for reaction, eV
k = rate constant, sec^{-1}
L = reactor length, cm
n_e = electron density, cm^{-3}
P = pressure, torr
S = cross section of plasmachemical reactor, cm^2
T = temperature, K
V = volumetric flowrate, $cm^3\ min^{-1}$
v_e = electron velocity, cm sec^{-1}
W = specific input power, W cm^{-1}
Z_i = conversion of i component

Greek Letters

β_i = relative concentration of i component
δ_R = factor for calibrating flowrate change by chemical reaction
ε = specific energy, J
σ^e_{diss} = effective cross section of collision for dissociation by direct electron inpact, cm^2
τ = residence time, sec

Superscripts

HCN = hydrogen cyanide
N = atomic nitrogen
N_2 = nitrogen molecule
Pr = product
R = reaction
0 = initial state

Subscripts

e = electron
R = reaction

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